

The University of Chicago

THE HYDROLYSIS
OF THE CHLORINE DERIVATIVES
OF METHANE UNDER HIGH
TEMPERATURES AND
PRESSURES

A PART OF A DISSERTATION SUBMITTED TO
THE FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1935

By

FREDERIC TAYLOR GURNEY

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INTRODUCTION

As early as 1881 the hydrolysis of carbon tetrachloride by water alone was reported¹ and five years later the same reaction with chloroform and methylene chloride was carried out,² but up to the present, there has been no systematic study of the hydrolysis of the chlorine derivatives of methane. It was to accomplish this end that the present investigation was undertaken. The previous experimental work was done in sealed glass tubes without definite information as to the temperature and pressure. With the modern development of high-pressure technique and the improvement made by Dr. A. von Grosse³ in the design of a glass reaction vessel having a long capillary opening, these experiments are now possible under conditions which afford definite temperatures and accurately known pressures. Materials which would otherwise leave the reaction vessel and, if corrosive, also attack the steel bomb at high temperatures and pressures, can thus be used and the reaction products determined qualitatively.

It was, of course, well known that the rate of hydrolysis of these compounds under ordinary conditions was very low indeed, especially for the more highly chlorinated products, as shown by Doughty⁴ who found no hydrolysis of carbon tetrachloride even after it had stood twelve weeks at room temperature and atmospheric pressure. Benrath did indicate an increase in this rate in the case of carbon tetrachloride and chloroform⁵ when the aqueous mixture was exposed to sunlight or ultraviolet radiation.

In 1886 Andre reported the formation of formic acid and carbon monoxide by treating ten volumes of water with one volume

¹H. Goldschmidt, Ber., 14, 928 (1881).

²M. Andre, Jahresbericht, volume for 1886, p. 627.

³L. A. Johnson, "An Attempt to Measure Gaseous Diffusion Under Pressure," Master's thesis, University of Chicago, 1932.

⁴H. Doughty, J. Am. Chem. Soc., 39, 2685 (1917).

⁵A. Benrath, Annalen, 382, 224 (1911).

of chloroform¹ for several hours at 225°, and also the same products, with methyl chloride and methyl alcohol in addition, by long heating of methylene chloride² with water at 180°. In the following experiments, with the temperature and pressure controlled, five hours or less was found to be sufficient for the reaction.

The four chlorine derivatives of methane; carbon tetrachloride, chloroform, methylene chloride and methyl chloride are treated with water, under similar conditions of temperature and pressure, and the reaction products identified and determined.

¹Andre, op. cit.

²Andre, C. r., 102, 1474 (1886).

EXPERIMENTAL PART

Apparatus

The apparatus used in this work consisted of a steel bomb, an electric furnace, and several pyrex glass cylinders 35 cm. long and 3.5 cm. in diameter, each having a hollow ground glass stopper with a 15 cm. capillary 1 mm. in diameter, coiled into a flat spiral and sealed on at the top of the stopper. Two small glass projections on the side of the stopper and on the neck of the cylinder made it possible to secure the stopper by means of two bronze wire springs attached to the stopper and the cylinder.

The bomb was of the type used by Ipatiev in his work on high-pressure reactions. It was made of Siemens-Martin steel, with an internal diameter of 4 cm., walls 1.5 cm. thick, and an internal depth of 39 cm. The cap was joined to the bomb by an annealed copper gasket and held in place by four 2-cm. bolts. The cap was fitted with a manometer of the Bourdon type, reading from 0 to 200 kg./cm.² and with a needle valve and union for connection with a gas cylinder.

The furnace consisted of an iron pot wrapped with asbestos paper and wound with Nichrome ribbon. This was surrounded by a sheet iron shell; the space between the shell and the pot was packed with infusorial earth. The part of the shell which projected above the pot was lined with asbestos paper to a thickness of 3 cm. Above the pot was placed a plate with a hole in the center, just large enough to admit the steel bomb which was supported in the furnace by the boltheads resting on the plate. Those parts of the bomb fittings which projected above the furnace were wrapped with asbestos cord to minimize heat losses. A bath of solder melting at about 184° was used to establish thermal contact between the iron pot and the bomb. An open tube was inserted diagonally through the wall of the furnace to allow the temperature of the bath to be taken with a thermometer. Enough solder was used to bring the level almost to the plate which supported the bomb.

The furnace was operated on a 220 volt A.C. circuit with

external resistances for control. A thermostatic device was also employed to keep the temperature of the bath constant during a run. This consisted of a narrow steel cylinder closed at one end and so fixed in the bottom of the solder bath that it extended 34 cm. up into the solder and that the open end projected a few centimeters below the furnace. In this cylinder was an invar steel rod, free to move, but supported by one end of a lever, the other end of which it forced up to make the contact whenever the steel cylinder cooled and contracted sufficiently to push the rod down. When the contact was made, the carbon filament in a small bulb at the top of an N shaped glass tube heated and expanded the nitrogen in this bulb, pushing the mercury in the lower part of the tube up the inclined portion to make contact with the mercury standing in the other upright portion of the tube. This closed system carried the 220 volts required for the furnace and prevented any oxidation or other difficulty that might be caused by the frequent make and break of the higher voltage circuit if the contacts were exposed to the air. By this means it was possible to keep the temperature of the solder bath constant within 2° C.

Procedure

In the case of methyl chloride special precautions which will be described below were necessary, but in the work with carbon tetrachloride, chloroform, and methylene chloride, the following procedure was used.

The glass cylinder was filled with 170 to 190 cc. of distilled water and weighed accurately on a large balance having a reproducible sensitivity greater than 4 mg. with a load of 400 g. Then 5 to 10 g. of the compound to be hydrolyzed, an amount small enough to insure complete reaction, was introduced through a long stemmed funnel reaching almost to the surface of the liquid in the cylinder. The mixture was then gently agitated until the last visible traces of the heavier liquid had disappeared from the surface of the water and any losses due to evaporation thus reduced to a negligible amount. The tube was then weighed again and the amount of material added, determined by difference.

The cylinder containing the materials to be examined was then carefully lowered into the steel bomb, in the bottom of which had been placed a small pad of asbestos to prevent any mechanical shock or excessive heating at the region of contact. The cap of

the bomb was then put in place, with the copper gasket making the contact between the two parts. After the whole was made tight by means of the four bolts and nuts, connection was made with a tank equipped with a high range pressure regulator, and filled with nitrogen under pressure of 2000 or more lbs./sq.in., and the gas was slowly admitted until a pressure of about 30 kg./cm.² was built up in the bomb. The solder bath was previously raised to a temperature of about 300° C. and the bomb was then lowered gradually into the bath; the pressure of nitrogen from the tank was continually increased until the bomb and the contents reached the temperature at which it was desired to make the run. The purpose was to admit the gas at such a rate that the pressure outside the glass vessel would increase more rapidly than the pressure of vapor inside and there would be a steady flow of gas through the capillary into the glass vessel, thus preventing the escape of any of the vapor. The needle valve on the bomb and that on the tank were then closed and the bath maintained at the desired temperature for the period of the run.

At the end of this time the bomb was removed from the bath and allowed to stand for several hours, usually overnight, until it cooled to room temperature. This gave better results than when the bomb was rapidly cooled in a stream of water and then placed in a freezing mixture of salt and ice. Due to the condensation of most of the gas in the glass vessel the pressure inside would fall more rapidly than that outside and would thus prevent any flowing out.

After a time sufficient to allow the whole system to come to room temperature, the gas in the bomb was released through a line suitably equipped to collect and determine quantitatively any of the reaction products which might come off as the pressure decreased until equal to that of the atmosphere. The bomb was then opened and the solution in the glass vessel given further treatment as required for each particular compound studied. In each case a very slight corrosion of the under surface of the copper gasket was noticed.

In the case of the gas methyl chloride, a special procedure was required. The volume of water employed was usually somewhat smaller than that taken for the other materials examined, since it was necessary that it be frozen, and that sufficient room be left in the center of the glass cylinder to introduce a narrow

tube containing the methyl chloride. The proper quantity of water was introduced in small amounts and frozen solid each time in a mixture of salt and ice. During the freezing, air was passed into the water through a narrow glass tube reaching almost to the bottom of the glass vessel, thus preventing fracture of the container due to the expansion of the water when solidifying and also leaving a long narrow opening, well down into the cylinder.

The cylinder was kept at a temperature of -15° C. in the salt and ice mixture while a 12 cm. pyrex tube 1 cm. in diameter, sealed and rounded off at the bottom, was immersed in liquid nitrogen and filled with methyl chloride which froze solid in the lower portion but remained liquid at the surface. The tube was previously weighed as taken from the nitrogen bath and again under the same conditions filled with methyl chloride, thus giving the weight of methyl chloride. The thin film of ice on the weighing tube did not vary more than a few milligrams, so that in a total weight of 5 to 10 g. of methyl chloride there was no appreciable error.¹ After the weighing, the tube was again cooled in the liquid nitrogen and then introduced into the glass cylinder containing the ice. This was immediately put into the bomb and kept under a slowly increasing pressure of nitrogen which prevented the escape of the methyl chloride vaporized in the glass vessel. The bomb was placed in water which was gradually heated to a temperature of 70° or 80° C. during the course of ten or fifteen minutes. The bomb, still connected to the nitrogen tank was then dried and lowered into the previously heated solder bath while the rate of flow of gas from the tank was increased until the whole system came to the temperature at which it was desired to make the run. At this point, the valve on the bomb was closed, and this temperature was maintained until the end of the run when the bomb was removed and allowed to cool in the air.

The variations in the subsequent procedure for each compound hydrolyzed, together with the tabulation of results for a number of runs, are given below under the appropriate headings. In each case, the liquid used for the hydrolysis was obtained in the purest available form from the storeroom and then redistilled.

¹This method was used by A. Archibald and I. McIntosh in their low temperature work with dimethyl ether. J. Am. Chem. Soc., 85, 922 (1904).

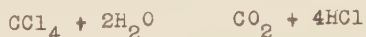
Hydrolysis of Carbon Tetrachloride

In the case of carbon tetrachloride the gaseous reaction product was passed through a train consisting of three Drechsel washbottles and a Geissler bulb. The first washbottle contained water, colored with methyl orange to detect hydrogen chloride; the second, a known amount of concentrated potassium hydroxide; the third, concentrated sulfuric acid to dry the gas before it passed into the weighed Geissler bulb in which traces of carbon dioxide, unabsorbed in the second washbottle were determined. Another washbottle filled with barium hydroxide was then placed as the last member of the train to show whether any carbon dioxide was passing through, unabsorbed by the potassium hydroxide.

The methyl orange in the first bottle showed no color change indicating the absence of hydrogen chloride from the gas. The potassium hydroxide in the washbottle was titrated and the amount of carbon dioxide determined by differential titration, using the phenolphthalein and methyl orange endpoints. To the amount thus found was added that calculated from the increase in weight of the Geissler bulb. At first low results were obtained because of the gas which remained dissolved in the solution in the reaction tube, but this difficulty was overcome by quickly removing the glass vessel from the bomb as soon as the system reached atmospheric pressure, attaching it directly to the line and bubbling carbon dioxide free air through the solution, thus removing the carbon dioxide and sweeping out the system. The volume of the solution was then measured and samples titrated with standard N/10 sodium hydroxide to determine the acidity.

The results of the hydrolysis with the amount of material and conditions used in each run are given in Table 1. A quantity as large as that taken in Run No. 1, 23 g. was found to leave a residue, 6 g. in this case, of unhydrolyzed carbon tetrachloride. In subsequent runs smaller quantities were taken and the reaction went to completion even in an hour and a half.

The complete hydrolysis of carbon tetrachloride may be represented by the following equation:



The results in the table were calculated on this basis.

TABLE 1
HYDROLYSIS OF CARBON TETRACHLORIDE

Run	1	2	3	4
Time in hours.	4 1/4	3	4 1/2	1 1/2
Temp. in ° C	240	260	260	260
Press. in kg./cm. ² . . .	100	75	75	65
Grams CCl ₄	23.06	5.838	6.003	5.847
Moles CCl ₄	.1496	.0379	.0390	.0380
Mole per cent HCl . . .	55.0	88.2	90.5	93.0
Mole per cent CO ₂ . . .	36.7	40.5	97.0	97.6

Hydrolysis of Chloroform

With this material a different treatment was necessary to determine the products of the reaction. After the period of heating, the bomb was allowed to cool to room temperature and the gas released through a train composed of the following parts. The first and second members were the same as those used in the hydrolysis of carbon tetrachloride, and then an electrically heated combustion tube filled with copper oxide was introduced. This was maintained at a temperature of 500° C. and from it the gas was passed through another potassium hydroxide washbottle and, finally, through the barium hydroxide solution as a check on the absorption in the line.

There was very little carbon dioxide found in the first potassium hydroxide bottle, but the combustion yielded considerable quantities, ranging almost to 90 per cent of the chloroform used. The acidity of the solution in the glass reaction vessel was found to be definitely higher than that corresponding to the chlorine content. Qualitative tests¹ performed on samples of this solution and confirmed with knowns and blanks showed that it con-

¹S. P. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, New York, 1904, I, 83.

tained formic acid. This was determined by the Jones method¹ and the data thus obtained were used to determine the acid present due to the chlorine and not the carbon of the chloroform.

The solution from several runs with chloroform was neutralized with sodium hydroxide and concentrated by evaporation for the purpose of preparing some pure formic acid from the chloroform. It was found that the formate and chloride could not be separated by fractional precipitation because the two crystallized out together in such a way as to make the procedure ineffective. Since with water, each of the two acids forms a constant boiling mixture having very nearly the same boiling point as the other, fractional distillation was also rather unpromising as a means of separation. The widely differing chemical properties of the two in respect to their dissociation, furnished a ready means by which to accomplish the end desired.

A slight excess of orthophosphoric acid was added to 500 cc. of the solution of one per cent sodium formate and approximately 15 per cent sodium chloride in water. The mixture was distilled with steam, to keep sufficient liquid in the distilling flask. Hydrochloric acid is practically, completely dissociated, but the constant for formic acid is 2.14×10^{-4} , and that for the first hydrogen of orthophosphoric acid is 1.1×10^{-2} . Thus the phosphoric acid can displace the formic acid from its salt, while it has very little effect on the chloride. This procedure made it possible to recover 85.5 per cent of the formic acid with no more than a slight trace of chloride, by means of fractional distillation, a small amount of 73 per cent formic acid was prepared.

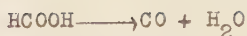
The results of the experiments on chloroform, including the amount of material, and conditions used in each run are given below in Table 2. The hydrolysis of chloroform may be represented by the following equation.



The decomposition of the formic acid is hastened, however, by the hydrochloric acid, as shown by Branch² and a further reaction takes place in accord with the following equation.

¹E. P. Treadwell and W. P. Hall, "Analytical Chemistry," John Wiley and Sons, New York, 1919, II, 253.

²G. E. K. Branch, J. Am. Chem. Soc., **37**, 2316 (1915).



This reaction may also be reversible under these conditions, and a certain amount of formic acid produced from carbon monoxide and water.¹ These equations furnish the basis for the calculation of the results given in Table 2.

TABLE 2
HYDROLYSIS OF CHLOROFORM

Run	1	2	3	4
Time in hrs.	3	2 1/2	5	3
Temp. in ° C	225	255	255	255
Press. in kg./cm. ² . . .	68	108	127	113
Grams CHCl ₃	9.368	9.784	5.681	5.588
Moles CHCl ₃	.0781	.0818	.0475	.0467
Mole per cent HCl . . .	88.9	90.0	95.0	100
Mole per cent CO	88.9	81.3	75.5	65.7
Mole per cent HCOOH. . .	4.5	17.7	24.6	35.1
Total.	93.4	99.0	100.1	100.8

Hydrolysis of Methylene Chloride

In this experiment the same procedure as that for the hydrolysis of chloroform was followed at first, to determine whether any carbon dioxide and carbon monoxide were formed. Only a small amount of carbon dioxide, less than 1 mole per cent, was produced while approximately 4 per cent of the original material was recovered as CO. There was also a slight deposit of carbon in the glass reaction vessel. This, however, was less than .5 per cent.

When the solution remaining in the glass tube was examined, it was found that 2.14 equivalents of acid were formed for each mole of methylene chloride used in the reaction. The chlorine in

¹Ibid.

the solution was also determined by titration with standard N/10 silver nitrate solution using potassium dichromate as indicator. This showed an average of 1.93 equivalents per mole of methylene chloride used.

Samples of the solution were then treated with N/10 potassium permanganate solution as in the previous experiments. Even moderately constant results could not be obtained unless 45 minutes was allowed for the oxidation, while previously 10 minutes was sufficient to give good checks.

Also a faint odor of formaldehyde from the solution was noticed and by oxidation with hydrogen peroxide,¹ a quantity of formic acid equivalent to approximately 5 per cent of the original material, was produced.

Several runs were also made using a cold trap in a carbon dioxide and acetone bath. As the gas came from the bomb it was first passed through a drying tube filled with anhydrous sodium sulphate and then through the cold trap and the same train as before, but nothing was found to collect in this vessel.

Portions of the liquid from the glass vessel were also examined for dissolved gasses. A measured volume of the solution was neutralized with an equivalent amount of 1.8 N sodium hydroxide and was then refluxed while any gas coming off at the top of the reflux condenser was led down through another water cooled condenser and out through a trap cooled in ice water and then one in a carbon dioxide and acetone solution. There was no deposit in either of the vessels, although the solution was boiled for half an hour.

The water was then drained from the reflux condenser and the liquid allowed to distill over. The first drops collected were identified as methyl alcohol by the odor and the resorcinol test.²

A measured volume of the solution from several different runs was evaporated without neutralization and a syrupy, caramel-like substance was found to deposit in the flask. While still liquid, this residue was transferred to a small beaker and placed in a vacuum dessicator containing pellets of potassium hydroxide

¹A. F. Holleman, "A Textbook of Organic Chemistry," John Wiley and Sons, New York, 1925, p. 126.

²Mulliken, op. cit., p. 171.

and a beaker of concentrated sulfuric acid. The beaker was then evacuated for four days. After the hydrogen chloride was thus removed, the material was found to have a caramel-like odor as well as appearance. A similar product from carbon monoxide and hydrogen is described by Vogel.¹

A determination of the carbon and hydrogen by combustion of this material showed 39.1 per cent carbon and 4.4 per cent hydrogen. While the hydrogen is low, the carbon content would still indicate the composition of a polymer of formaldehyde, (CH₂O), which is 40.0 per cent carbon and 6.7 per cent hydrogen.

The same conclusion is reached from examination of the properties of the material. When it is extracted with alcohol an insoluble white powder is left. This is also insoluble in ether and in cold water, but will dissolve in hot water and in dilute alkali. The material melts at 150-2° and sublimes. These properties are described by Orloff² as those of trioxymethylene.

On the sides of the beaker fine, white needles were formed in small amounts. These melted at 57-9° C which is very close to the melting point of the compound α trioxymethylene, formed from formaldehyde under more or less similar conditions and described by Fratesi³ as melting at 60-1° C. Another type of white crystals somewhat thicker and occurring in clusters was formed after prolonged drying over sulfuric acid. These melted at 94° C and were soluble in water. This material is similar to one of the polymers of formaldehyde described by Seyewitz and Gibello.⁴

The hydrolysis of methylene chloride may result in the primary formation of the unstable formaldehyde hydrate in accordance with the following equation.



The hydrate may then split off water to give formaldehyde



or two molecules may undergo an inter molecular oxidation and

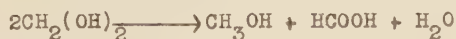
¹Vogel, Helv. chim. acta 11, 370 (1928).

²J. E. Orlov, "Formaldehyde," J. A. Barth, Leipzig, 1909, p. 27.

³L. Fratesi, Gazz. chim. ital., 14, 139.

⁴U. Seyewitz and S. Gibello, C. r., 138, 1225 (1904).

reduction to give methyl alcohol, formic acid and water as follows:



In Table 3 are given the results of the hydrolysis and the time, temperature, pressure and amount of material used in each run. Upon the basis of the above equations it will be seen that the sum of the equivalents of the formaldehyde polymer, the formic acid, the formaldehyde and the equivalent alcohol are approximately equal to the number of equivalents of methylene chloride taken in each case. The complicated carbohydrate chemistry and involved procedure required for a thorough study of this complex mixture seemed beyond the scope of the present investigation and the examination was not carried further.

TABLE 3
HYDROLYSIS OF METHYLENE CHLORIDE

Run	1	2	3	4
Time in hours	2	2	2	2
Temp. in ° C	250	250	251	247
Press. in kg./cm ² . . .	116	99	100	90
Wt. CH ₂ Cl ₂ in grams . .	16.73	16.89	14.46	14.39
CH ₂ Cl ₂ in moles	.197	.199	.170	.169
Equiv. of Acid per mole	2.08	2.13	2.14	2.14
Equiv. of Cl per mole	1.80	1.92	1.96	1.92
Equiv. of Oxid. by H ₂ O ₂	.04	.02	.05	.02
Equiv. Oxid. by KMnO ₄	.56	.75	.77	.72
Equiv. in Gas			.04	.05
Equiv. in Residue		.56		.54

Hydrolysis of Methyl Chloride

The procedure followed during the release of the gas from the bomb after the hydrolysis of methyl chloride was exactly the same as that used with methylene chloride. The treatment of the solution in the glass vessel was also carried out in the same way as in the previous experiment, with the exception that liquid nitrogen was used instead of carbon dioxide and acetone as the cooling agent for the cold trap.

No carbon dioxide was collected in the first potassium hydroxide washbottle which came just before the combustion furnace in the line. Neither was there any carbon dioxide collected in the second potassium hydroxide washbottle. Thus, with no carbon dioxide or carbon monoxide formed by the hydrolysis, it was possible to determine the amount of the unhydrolyzed methyl chloride in the gas, either by freezing it out in the liquid nitrogen trap, or by combustion.

A deposit of solid methyl chloride was also formed in the cold trap while the solution was refluxed before being distilled. The weight of the methyl chloride in the cold trap was always taken just as it began to melt, so that the temperature was the same in each case. After the weighing, when the vessel warmed up sufficiently, the liquid evaporated, giving off a stream of gas which was found to burn with the characteristic green flame.

The results of the hydrolysis and the conditions and amount of methyl chloride used for each run are given below in Table 4. The data for the methyl chloride in the gas, in Runs 2, 3 and 4 were obtained by combustion. The data for the amount of methyl chloride dissolved, but unhydrolyzed, in Run 3, were calculated from the solubility of this gas in water, but are in relatively good agreement with the experimental results from the other runs.

The hydrolysis of methyl chloride may be represented by the following equation.



The methyl alcohol formed may, however, react with another molecule of methyl alcohol with the elimination of water, or may react with methyl chloride, forming methyl ether, as indicated in the

equations



TABLE 4
HYDROLYSIS OF METHYL CHLORIDE

Run	1	2	3	4
Time in hours	2	2	2	2
Temp. in ° C	255	255	255	255
Press. in kg./cm ²	83	80	87	76
Grams of CH ₃ Cl	9.34	7.65	7.60	12.95
Moles of CH ₃ Cl	.185	.151	.150	.256
Final vol. in cc.	134	131	174	140
Mole per cent HCl	71.4	71.4	76.3	67.4
Mole per cent CH ₃ OH . . .	58.7	60.0	66.1	53.5
Per cent unhydrolyzed . .	22	24	19	29
Grams CH ₃ Cl Dslvd. . . .	.6	1.2	1.0	2.2
Per cent CH ₃ Cl Dslved . .	6.9	15.5	13.7	17.3
Per cent CH ₃ Cl Gas. . . .	14.6	8.0	5.1	11.3
Total	92.8	95.3	95.1	96.0

These equations may account for the slightly low results obtained for the alcohol, produced in the hydrolysis. The determination was made by distilling about 60 per cent of the liquid in the flask, diluting the distillate to 100 cc. and then oxidizing samples from this solution in 12 N sulfuric acid with a standard potassium dichromate solution as suggested by Kistler,¹ with the exception that the end point was not determined electrometrically, but by the use of the potassium ferricyanide indicator and spot plate.

¹S. S. Kistler, Science, 69, 457 (1929).

SUMMARY

By an improved technique in high pressure work and the use of a recently designed glass reaction vessel, open only through a long capillary tube coiled in a flat spiral above the stopper, it is now possible to employ highly reactive and volatile materials under carefully regulated conditions of temperature and pressure, hitherto impossible. The apparatus consisted of the reaction vessel placed within a steel bomb with pressure gauge and needle valve, and an electrically heated solder bath.

Different pressures, from 60 to 120 atmospheres and temperatures from 200° to 300°C, usually 250°, were used. The hydrolysis of the chlorine derivatives of methane, i.e. carbon tetrachloride, chloroform, methylene chloride, and methyl chloride, was carried out with this apparatus, and the reaction products identified and determined.

With approximately 250 moles of water per mole of carbon tetrachloride, at 260°C and a pressure of 65 kg./cm², only an hour and a half was required for complete hydrolysis as indicated in the following equation.

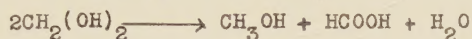
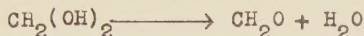
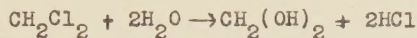


With the same relative amounts of chloroform and water, at the same temperature, but under a pressure of 113 kg./cm² complete hydrolysis occurred within three hours. The chloroform was hydrolyzed to carbon monoxide, formic acid and hydrochloric acid in accord with the following equations.

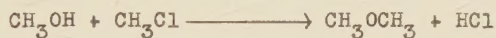
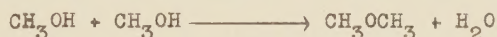
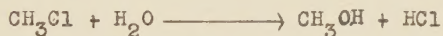


A mole ratio of 50 to 1 of water and methylene chloride was found to give complete hydrolysis within two hours at 250°C and 90 kg./cm². This material gave the most complicated reaction products. They consist of methyl alcohol, formic acid, formaldehyde and various polymers of formaldehyde. A further study of this complex mixture with its numerous possibilities for condensation and inter molecular oxidation and reduction reactions which

involve the complicated chemistry of the carbohydrates, was not deemed to be within the scope of this investigation. The hydrolysis may be indicated by the following equations.



With 70 moles of water per mole of methyl chloride at 255°C and under a pressure of 87 kg./cm² approximately 80 per cent hydrolysis occurred within two hours. The material was hydrolyzed to methyl alcohol and hydrochloric acid with also the possible formation of methyl ether as shown in the following equations.



In conclusion it is desired to express sincere appreciation of the counsel and guidance given by Dr. A. von Grosse in the course of these experiments.

